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Calculation of Basic Parameters Necessary for Quantum Chemical Calculations on Boron-Containing Molecules. II. $(pp|pp)_{B^-}$ and Valence State Electron Affinities of B^-.

by

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ABSTRACT

A modified one-center electron repulsion integral (pp|pp) for B^- which takes into account correlation effects has been calculated. For these calculations it was necessary to evaluate the electron affinities of B^- to form $B^=$ in various valence states. This was done by adapting an existing rigorous extrapolation procedure to valence state calculations.

The electron repulsion integrals were calculated by expansion of the energies of B, B^- and $B^=$ as a function of spectroscopic term values. The value for $(pp|pp)_{B^-}$ calculated in this manner, 4.737 ev, and the value calculated using the Pariser-Parr approximation, (pp|pp) = I-A = 4.015 ev, are quite close. This is especially gratifying in view of the fact that the two calculations are independent and that each calculation depends on extrapolated values for the electron affinities of B^- in completely different valence states.

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Introduction

As part of a general program on quantum chemical calculations on boron-containing molecules, it has been necessary to calculate modified values of electron repulsion integrals for boron atoms. In part I [1], the modified value for the one-center $(pp|pp)_B$ was calculated following the method of Julg [2] by expansion of the energies of the various valence states in terms of spectroscopic term values.

In this paper we describe the calculations of the one-center $(pp|pp)_B$- and also the calculations of the various valence state electron affinities of B^- necessary for the calculation of $(pp|pp)_B$-.

Calculations

Method I Estimation by Pariser-Parr Approximation

The simplest method to evaluate $(pp|pp)_B$- in the valence state $sp^2\pi$ is to use the expression derived by Pariser and Parr [3] for evaluating $(pp|pp)_C$ in the same valence state $sp^2\pi$:

$$(pp|pp)_C = I_C - A_C$$

where I_C = ionization potential of the $2p\pi$ e on carbon in the state $sp^2\pi$

A_C = electron affinity of carbon in the state $sp^2\pi$ to form C^- $sp^2\pi^2$

$(pp|pp)_{B^-} = I_{B^-} - A_{B^-}$

where I_{B^-} = ionization potential of the $2p\pi$ e on B^- in the state $sp^2\pi$

A_{B^-} = electron affinity of B^- in the state $sp^2\pi$ to form $B^=$ $sp^2\pi^2$

I_{B^-} $sp^2\pi \rightarrow sp^2$ has been calculated both by Jaffe [4] and Pilcher and Skinner [5]. The two values are very close 1.061 ev [4] or 0.96 ev.[5]

However, the electron affinity for B^- in its ground state or in its valence states had never been previously calculated. We have calculated the valence state electron affinities of B^- following a suggestion by Rohrlich [6] that we use the extrapolation procedure of Edlén [7] and extrapolate from the ionization potentials of the next three isoelectronic atoms in the same valence states as the B^-.

Calculation of electron affinity of B^- $(sp^2\pi)$ to form $B^=$ $(sp^2\pi^2)$

We used the formulas derived by Edlén [7]

$$T_o = 3T_1 - 3T_2 + T_3 + Q$$

$$Q = \frac{3(T_1 - 2T_2 + T_3 - 2R/n^2)\,(-T_1 + 2T_2 - T_3 + 6R/n^2)}{T_1 - 4T_2 + 3T_3 - 12R/n^2}$$

where T_o is the electron affinity in terms of the ionization energies T_1, T_2, T_3 of the first three members of the isoelectronic series, and n is the principal quantum number.

$B^= (sp^2\pi^2) \rightarrow B^- (sp^2\pi)$ $\qquad R/2^2 = 3.408$ ev

For T_1, T_2 and T_3 we have used

T_1 C^- $sp^2\pi^2$ = 0.03 ev
T_2 N $sp^2\pi^2$ = 11.957 ev
T_3 O $sp^2\pi^2$ = 30.891 ev

T_1, T_2 and T_3 for all the electron affinity calculations in this paper have either been taken directly from the papers of Jaffe and of Skinner or have been estimated by us from the tables of valence state promotion energies contained in these papers.

$$A_{B^-} = -2.954 \text{ ev}$$

$$B^- (sp^2\pi) \rightarrow B^{=} (sp^2\pi^2)$$

$$\therefore (pp|pp)_{B^-} = I_{B^-} - A_{B^-}$$

$$= 1.061 \text{ ev} - (-2.954 \text{ ev})$$

$$= 4.015 \text{ ev.}$$

Method II $(pp|pp)_{B^-}$ Calculation by the More Exact Method of Julg

To calculate $(pp|pp)_{B^-}$ by this method, it is necessary to expand the energies for various valence states of B, B^- and $B^{=}$ or those of B^+, B, B^- as a function of the various spectroscopic term values as indicated in the paper of Moffitt [8].

The expressions for $B^{=}$, B^-, and B are obtained from the following expansions

$B^{=}$	sx^2yz	$= (E_i+2\alpha+J_{xx})(1-\epsilon)$
B^-	$sxyz$	$= E_i+\alpha$
B	syz	$= E_i(1+\epsilon)$

$$B^{=} \quad sx^2yz = I_s + 2I_x + I_y + I_z + 2J_{sx} + J_{sy} + J_{sz} + 2J_{xy} + 2J_{xz} + J_{xx} + J_{yz} - K_{sx} - \tfrac{1}{2}K_{sy} - \tfrac{1}{2}K_{sz} - K_{xy} - K_{xz} - \tfrac{1}{2}K_{yz}$$

$$B^{-}_{sxyz} = I_s + I_x + I_y + I_z + J_{sx} + J_{sy} + J_{sz} + J_{xy} + J_{xz} + J_{yz}$$
$$- \tfrac{1}{2}K_{sx} - \tfrac{1}{2}K_{sy} - \tfrac{1}{2}K_{sz} - \tfrac{1}{2}K_{xy} - \tfrac{1}{2}K_{xz} - \tfrac{1}{2}K_{yz}$$

$$B_{syz} = I_s + I_y + I_z + J_{sy} + J_{sz} + J_{yz}$$
$$- \tfrac{1}{2}K_{sy} - \tfrac{1}{2}K_{sz} - \tfrac{1}{2}K_{yz}$$

$$E_i = I_s + I_y + I_z + J_{sy} + J_{sz} + J_{yz} - \tfrac{1}{2}K_{sy} - \tfrac{1}{2}K_{sz} - \tfrac{1}{2}K_{yz}$$

$$\alpha = I_x + J_{sx} + J_{xy} + J_{xz} - \tfrac{1}{2}K_{sx} - \tfrac{1}{2}K_{xy} - \tfrac{1}{2}K_{xz}$$

where $J_{xx} = (pp|pp)_{B^-}$

$$(B^{=} - B^{-}) + (B - B^{-}) = J_{xx} - \varepsilon(2\alpha + J_{xx})$$

$$-A_{B^-} + I_{B^-} = J_{xx} - \varepsilon(2\alpha + J_{xx})$$

$$(B^{-} - B^{=}) + (B - B^{-}) = -(2\alpha + J_{xx}) + \cancel{\varepsilon(E_1 + 2\alpha + J_{xx})}$$

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$$A_{B^-} + I_{B^-} = -(2\alpha + J_{xx})$$

$$\therefore\ J_{xx} = (I_{B^-} - A_{B^-}) - \varepsilon\,(I_{B^-} + A_{B^-})$$

To calculate the necessary $B^{-} \rightarrow B^{=}$

$sxyz \quad sx^2yz$

we used

T_1	C^-	0.345 ev
T_2	N	12.373 ev
T_3	O^+	31.239 ev

$$A_{B^-} = -4.0065 \text{ ev}$$

$$B^{-}(sxyz) \rightarrow B^{=}(sx^2yz)$$

This gives

$$(pp|pp)_{B^-} = (I_{B^-} - A_{B^-}) - \varepsilon\,(I_{B^-} + A_{B^-})$$

$$= [0.892 - (-4.6005)] - \varepsilon\,[0.892 + (-4.6005)]$$

$$= 5.4925 + 3.7085\varepsilon$$

It is necessary to have one more equation for ε and $(pp|pp)_{B^-}$ as a function of different valence states of boron in order to evaluate ε. There are two alternant methods which can be used to obtain the second relationship.

1) $B^{=}$ sx^2yz

B^{-} sx^2z

B sxz

We have expanded this relation as we did the first one and the result is

$$(pp|pp)_{B^-} - 5\,(p\bar{p}|p\bar{p})_{B^-} = (I_{B^-}' - A_{B^-}') - \varepsilon\,(I_{B^-}' + A_{B^-}')$$

where $(p\bar{p}|p\bar{p})$ is an exchange integral and

$B^{-} \rightarrow B^{=}$ A_{B^-}'

sx^2z sx^2yz

$B^{-} \rightarrow B$ I_{B^-}'

sx^2z sxz

However, this relation could not be used because we lack the necessary valence state promotion energy for 0^+ to this valence state sx^2z from which to extrapolate A'_{B^-}.

2) There is an alternate method by which one can obtain a second relation between $(pp|pp)_{B^-}$ and ϵ .

$$B^- \quad sx^2y = (E_i + 2\alpha) + J_{xx}$$

$$I_1 \downarrow$$

$$B \quad sxy = (E_i + \alpha)(1 + \epsilon)$$

$$I_2 \downarrow$$

$$B^+ \quad sy = E_i (1 + 2\epsilon)$$

$$B^- \quad sx^2y = I_s + 2I_x + I_y + 2J_{sx} + J_{sy} + 2J_{xy} + J_{xx} - \tfrac{1}{2}K_{sy} - K_{sx} - K_{xy}$$

$$B \quad sxy \quad I_s + I_x + I_y + J_{sx} + J_{sy} + J_{xy} - \tfrac{1}{2}K_{sx} - \tfrac{1}{2}K_{sy} - \tfrac{1}{2}K_{xy}$$

$$B^+ \quad sy \quad I_s + I_y + J_{sy} - \tfrac{1}{2}K_{sy}$$

$$E_i = I_s + I_y + J_{sy} - \tfrac{1}{2}K_{sy}$$

$$\alpha = I_x + J_{sx} + J_{xy} - \tfrac{1}{2}K_{sx} - \tfrac{1}{2}K_{xy}$$

$$I_2 = B^+ - B = E_i + 2\epsilon E_i - E_i - \alpha - \epsilon E_i - \epsilon\alpha$$

$$= \epsilon E_i - \alpha - \epsilon\alpha$$

$$I_1 = B - B^- = E_i + \alpha + \epsilon E_i + \epsilon\alpha - E_i - 2\alpha - J_{xx}$$

$$= \epsilon E_i - \alpha + \epsilon\alpha - J_{xx}$$

$$\varepsilon\alpha \approx -\varepsilon I_2$$

$$I_2 - I_1 = -\alpha - \varepsilon\alpha + \alpha - \varepsilon\alpha + J_{xx} = -2\varepsilon\alpha + J_{xx}$$

$$J_{xx} = I_2 - I_1 - 2\varepsilon I_2$$

$$(pp|pp)_{B^-} = 8.33 - 0.20 - 2\varepsilon(8.33)$$

$$= 8.13 - 16.66\varepsilon$$

Equating $(pp|pp)_{B^-} = 5.4925 - 3.7085\varepsilon$

$$(pp|pp)_{B^-} = 8.13 - 16.66\varepsilon$$

$$8.13 - 16.66\varepsilon = 5.4925 - 3.7085\varepsilon$$

$$\varepsilon = 0.203644$$

$$(pp|pp)_{B^-} = 8.13 - 16.66\,(.203644)$$

$$= 4.737 \text{ ev}$$

Results

The values of $(pp|pp)_{B^-}$ by the two different methods

1° Pariser-Parr $(pp|pp)_{B^-} = 4.015$ ev

2° Julg $(pp|pp)_{B^-} = 4.737$ ev

are quite close. This is especially gratifying in view of the fact that the two calculations are independent and, that each calculation depends on extra-

polated values for the electron affinities of B^- in completely different valence states.

Appendix

The ground state electron affinity of B^- was also calculated to compare the magnitudes of the electron affinities in various valence states.

For this calculation the values of T_1 for C^-, T_2 for N and T_3 for O^+ were taken directly from the article of Elden [7].

The ground state electron affinity of B^- to form $B^=$ is -2.19 ev.

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